

Metal–selenium interactions. Crystal structure of binuclear [(¹*h*-iodo)-(²*h-m*-iodo) (triphenyl selenophosphorane–Se)mercury(II)]₂ complex

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Abstract. Reaction of mercury(II) diiodide with triphenyl selenophosphorane–Se (1:1 mole ratio) in acetone followed by recrystallisation of the product from chloroform formed crystals of stoichiometry {HgI₂(Ph₃PSe)}(1). Compound 1 exists as a centrosymmetric homobimetallic dimer, {Hg(*m*-I)I(Ph₃PSe)}₂, as monoclinic crystals of space group *P*2₁/*n*. The dimer comprises two *m*₂-iodo atoms that form unequal Hg–I bonds {2.8230(10), 3.1135(9) Å} and two equal terminal Hg–I bonds {2.6524(10) Å}. The Se atom of Ph₃PSe forms terminal Hg–Se bond {2.5914(11) Å} and thus the geometry about each Hg centre is distorted tetrahedral and the range of tetrahedral bond angles is 92.97(2) to 130.85(3)°, the largest being that of Se(1)–Hg(1)–I(1) and the shortest, I(2)–Hg(1)–I(2)*. Hg–Hg and I–I separations of {4.0930(11) Å} and {4.3097(15) Å} are more than the sums of their respective van der Waal radii {3.00 Å and 4.24 Å}.

Keywords. Binuclear complex; mercury(II) iodide; triphenyl seleno-phosphorane–Se; centrosymmetric; phosphine chalcogenides.

1. Introduction

The coordination chemistry of tertiary phosphine chalcogenides bearing S or Se donor atoms is important from the point of view of their interesting bonding properties and novel structures, as well as their application in catalysis and extractive metallurgy^{1,2}. Whereas molecular structures of several complexes of phosphine sulphides have been reported, there are only a few reports on those of metal complexes with tertiary phosphine selenides^{3–5}. The major reason for the paucity of studies on the structural chemistry of phosphine selenide complexes is the poor solubility of the complexes^{1,2}.

We have been interested in the spectral and structural chemistry of metal–sulphur interactions involving phosphine sulphides and other N, S donors derived from heterocyclic thiones and thiosemicarbazones^{6–21}. The work on phosphine selenide reactions with metal salts was undertaken both as an extension of our interest in the

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structural chemistry of metal–selenium interactions and their importance in metal–organic chemical vapour deposition²². In this paper, the crystal and molecular structure of mercury(II) diiodide complex with triphenyl selenophosphorane–Se is reported.

2. Experimental

2.1 Materials and techniques

Triphenylphosphine selenide (Ph₃PSe) was prepared by the oxidation of triphenyl phosphine (Ph₃P) using selenium metal (1:1 mole ratio) in benzene solvent¹. Mercury(II) iodide and Ph₃P were procured from standard firms.

The title complex was prepared as follows. A solution of Ph₃PSe (0.075 g, 0.220 mmol) in acetone (30 ml) was added to a solution of mercury(II) iodide (0.100 g, 0.220 mmol) in acetone (15 ml) and the contents were stirred for 5 h. The solution was filtered and allowed to solidify at room temperature. On recrystallisation from chloroform, colourless crystals were formed. Yield, 60(%); m.p. (°C) 222–225. Analysis: (C₃₆H₃₀Hg₂I₄P₂Se₂) Found C, 27.36, H, 2.25%; Calcd.: C, 27.16, H, 1.88%. The C, H elemental analyses were obtained using a Carlo–Erba 1108 microanalyser. Melting point was determined with a Gallenkamp electrically heated apparatus. IR spectra were recorded using KBr pellets on a Pye–Unicam SP3-300 Infrared Spectrophotometer in the range 4000–400 cm⁻¹.

2.2 X-ray data collection and reduction

A colourless prismatic crystal of {Hg(*m*-I)(Ph₃PSe)}₂(**1**) was mounted on a glass fibre and used for data collection. Cell constants and orientation matrix for data collection were obtained by least squares refinement of the diffraction data from 25 reflections in the range of 9.485 < *q* < 12.872° in an Enraf Nonius CAD 4 automatic diffractometer²³. Data were collected at 293 K using MoK_α radiation (*I* = 0.71073 Å) and by the *w* scan technique and corrected for Lorentz and polarisation effects²⁴. A semi-empirical absorption correction (*y*-scan) was made²⁵.

The structure was solved by direct methods²⁶ and subsequent difference Fourier maps, and refined on *F*² by a full-matrix least squares procedure using anisotropic displacement parameters²⁷. All hydrogen atoms were fixed in their calculated positions (C–H 0.93–0.94 Å) and were refined using a riding model. Atomic scattering factors were used from international tables for X-ray crystallography²⁸. Molecular graphics were taken from PLATON 98²⁹. A summary of the crystal data, experimental details and refinement results are listed in table 1.

3. Results and discussion

3.1 General comments

Mercury(II) is a soft Lewis acid and is known to prefer soft Lewis bases such as the ones containing S or Se donor atoms. The IR spectra of the ligand and the complex were different and the diagnostic *n*P=Se peak appears at 550 cm⁻¹ in the ligand and at 540 cm⁻¹ in the complex, supporting coordination by the ligand via the Se atom. The shift is small in view of the low sensitivity of the heavier Se atom to changes on coordination to

Table 1. Crystal data and structure refinement for (1).

Empirical formula	C ₃₆ H ₃₀ Hg ₂ I ₄ P ₂ Se ₂
Formula weight (M)	1591.24
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	
<i>a</i> (Å)	10.477(2)
<i>b</i> (Å)	13.525(3)
<i>c</i> (Å)	14.709(2)
<i>β</i> (°)	92.21(2)
Volume (Å ³)	2082.9(7)
<i>Z</i>	2
<i>D</i> _{calcd} (Mg m ⁻³)	2.537
Absorption coefficient (mm ⁻¹)	12.175
<i>F</i> (000)	1432
Crystal size (mm)	0.25 × 0.15 × 0.15
Theta range for data collection (°)	2.05 to 27.97
Index ranges	−13 ≤ <i>h</i> ≤ 13, 0 ≤ <i>k</i> ≤ 17, −19 ≤ <i>l</i> ≤ 0
Reflections collected	5208
Independent reflections	5023 [<i>R</i> _{int} = 0.0520]
Max. and min. transmission	0.980 and 0.662
Data/restraints/parameters	5023/0/208
Goodness-of-fit on <i>F</i> ²	0.934
Final <i>R</i> indices [<i>I</i> > 2 <i>s</i> (<i>I</i>)]	<i>R</i> 1 = 0.0427, <i>wR</i> 2 = 0.0765
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1923, <i>wR</i> 2 = 0.1009
Largest diff. peak and hole (eÅ ⁻³)	0.879 and −2.314

a metal centre. The structure has been solved by X-ray crystallography in order to establish the nature of the Hg–Se interaction.

3.2 Description of crystal structure of (1)

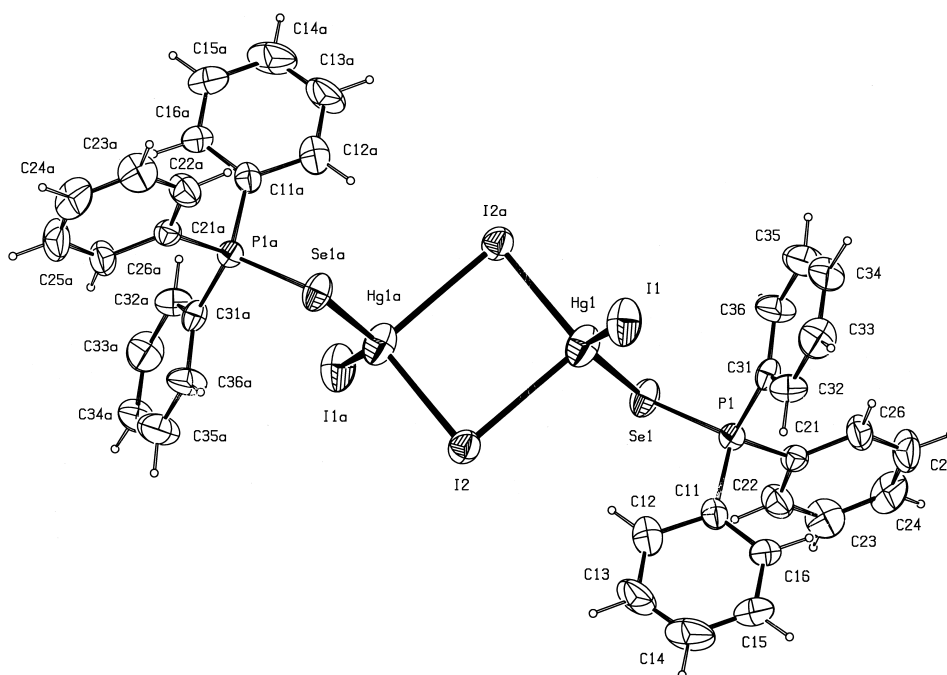
The atomic numbering scheme of {Hg(*m*-I)I(Ph₃PSe)}₂(1) is shown in figure 1. Table 2 contains important bond lengths and bond angles. The basic unit is {HgI₂(Ph₃PSe)} which dimerises to form 1 but there is no further interaction between the dimeric units.

One Se atom of the Ph₃PSe and two iodine atoms coordinate to Hg atom forming the unit {HgI₂(Ph₃PSe)} and this interacts with a second unit via iodine atoms to form the homobimetallic dimer [(I)(Ph₃PSe)Hg-(*m*-I)₂-Hg(Ph₃PSe)(I)] containing terminal Ph₃PSe and I groups in *trans* disposition. The angles around each Hg atom vary from 92.97(2) to 130.85(3)°, the largest being that of Se(1)–Hg(1)–I(1) and the shortest, I(2)*–Hg(1)–I(2). The geometry around each Hg centre is distorted tetrahedral. The shortest angle in the central unit Hg₂I₂ is that formed at the bridging iodine atoms, equal to 87.03(3)°. The angle Hg(1)–Se(1)–P(1) = 98.04(7)° at the Se atom is smaller than a tetrahedral angle due to the presence of a lone pair of electrons on the Se atom and also due to the multiple bond character of the P–Se bond. The geometry around each P atom is also distorted tetrahedral and the angles around the P atom vary from 106.1(4) to 112.7(3).

Table 2. Selected bond lengths [Å] and angles [°] for (1).

<i>Bond lengths</i>			
Hg(1)–Se(1)	2.5914(11)	I(2)–I(2)*	4.3097(15)
Hg(1)–I(1)	2.6524(10)	P(1)–Se(1)	2.173(3)
Hg(1)–I(2)*	2.8230(10)	P(1)–C(11)	1.800(10)
Hg(1)–I(2)	3.1135(9)	P(1)–C(21)	1.810(8)
Hg(1)–Hg(1)*	4.0930(11)	P(1)–C(31)	1.786(9)
I(2)–Hg(1)*	2.8230(10)		
<i>Bond angles</i>			
Se(1)–Hg(1)–I(1)	130.85(3)	Hg(1)*–I(2)–Hg(1)	87.03(3)
Se(1)–Hg(1)–I(2)*	107.49(3)	P(1)–Se(1)–Hg(1)	98.04(7)
I(1)–Hg(1)–I(2)*	112.61(3)	C(31)–P(1)–C(11)	111.0(4)
Se(1)–Hg(1)–I(2)	101.99(4)	C(31)–P(1)–C(21)	106.9(4)
I(1)–Hg(1)–I(2)	103.09(3)	C(11)–P(1)–C(21)	106.1(4)
I(2)*–Hg(1)–I(2)	92.97(2)	C(31)–P(1)–Se(1)	111.9(3)
Se(1)–Hg(1)–Hg(1)*	111.43(3)	C(11)–P(1)–Se(1)	112.7(3)
I(1)–Hg(1)–Hg(1)*	115.94(2)	C(21)–P(1)–Se(1)	107.8(3)

*Symmetry transformations used to generate equivalent atoms: $-x + 1, -y + 1, -z$.

**Figure 1.** The structure of $\{\text{Hg}(m\text{-I})(\text{Ph}_3\text{Pse})\}_2(\mathbf{1})$ showing the numbering scheme.

The Hg(1)–Se(1) bond distance {2.5914(11) Å} is longer than that found in the analogous compound $\{\text{HgCl}_2(\text{Ph}_3\text{PSe})\}_2(\mathbf{2})$ {Hg–Se = 2.527(3) Å}³ and these distances are much smaller than the sum of the van der Waal radii {3.40 Å} and also the sum of the radii of Hg²⁺ and Se²⁻ (3.00 Å)³⁰. The P(1)–Se(1) bond distance of 2.173(3) Å is close to that found in $\mathbf{2}$ {P–Se = 2.169(6) Å} and these distances are longer than that in free ligand

Ph_3PSe $\{\text{P–Se} = 2.106(1)\text{Å}\}^{31}$ and in turn all these coordinated and uncoordinated P–Se distances are smaller than the sum of the covalent radii of P and Se atoms $\{2.27\text{Å}\}^9$. Obviously the double bond character of P–Se bond in the free ligand is reduced in the coordinated ligand. The dimer comprises two m_2 -iodo atoms that form unequal Hg–I bonds $\{2.8230(10), 3.1135(9)\text{Å}\}$ and two equal terminal Hg–I bonds $\{2.6524(10)\text{Å}\}$. The Hg–Hg and I–I separations of $\{4.0930(11), 4.3097(15)\text{Å}\}$ are more than the sum of their van der Waal radii $\{3.00, 4.24\text{Å}\}$ respectively. The Hg–Hg separation in **2** is 3.87Å and obviously bulky iodine atoms in **1** push the Hg atoms outwards. The Hg–I bonds of the central Hg_2I_2 unit use p -orbitals for bonding and the terminal Hg–I and Hg–Se bonds use s - and p -orbitals.

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